This Week's Citation Classic

Chao K C & Seader J D. A general correlation of vapor-liquid equilibria in
hydrocarbon mixtures. *AIChE J.* 7:598-605, 1961.
[California Research Corp., Richmond, CA]

A general correlation of vapor-liquid equilibria (VLE) in hydrocarbon mixtures is developed. The vaporization equilibrium ratio is expressed in the form of a set of equations suitable for computer application. The correlation applies to hydrocarbons of various molecular types, including paraffins, olefins, aromatics, and naphthenes. Hydrogen in hydrocarbon mixtures is correlated. [The *SCI®* indicates that this paper has been cited in over 130 publications since 1961.]

K.C. Chao
School of Chemical Engineering
Purdue University
West Lafayette, IN 47907

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"Calculation of the vapor-liquid equilibrium (VLE) is basic to the design of separation operations such as distillation, which is practiced in oil refining and petrochemical processes. The separation achieved in the designed operation is directly controlled by the VLE factors used in the calculation.

"Up to the time of our work, VLE calculations were done by design engineers using a large volume of charts of VLE K-factors in slide rule operations. The charts, though voluminous, were nevertheless adequate only for paraffin hydrocarbons. Separate corrections were introduced for the presence of aromatic hydrocarbons, and for other effects. The charts with the various corrections were still unsatisfactory to meet the needs of new technology such as hydrofining.

"Instead of developing additional correction factors, we decided to take a new approach and apply the fundamental thermodynamics principles of fluid phase equilibria. The fundamental principle of equality of fugacity had been known for a long time but its application had been restricted to ideal solutions of gases in contact with ideal liquid solutions. But many new results had been developed during the preceding decade or so in the understanding of gas mixtures and liquid solutions. Time was ripe for the new information to be put together for an engineering application.

"Our new work was therefore in the nature of a synthesis, the elements of which were Hildebrand's regular solution theory, Pitzer's corresponding state principle, and Redlich's equation of state. By putting these factors together we could make purely predictive calculations for many mixtures in excellent agreement with data. But for many other mixtures, notably those containing light gases, the new method was inapplicable unless extended, which we accomplished by making use of experimental data. The liquid standard state was extended to hypothetical states, and new parameter values in Hildebrand's theory were determined. It was the use of experimental data in this connection that made our work a correlation.

"Our new method would have been hopelessly complicated if implemented by slide rule calculations. Fortunately, electronic digital computers became available which greatly promoted its use.

"We presented our work at the annual meeting of the American Institute of Chemical Engineers (AIChE) in 1959. Reception of it was immediate. Many companies adopted it and the Natural Gas Processors Association prepared a computer program to distribute to its members. For some years it came close to being an 'industry standard' in the gas processing industry. But when submitted to the *AIChE Journal* for publication, the manuscript suffered outright rejection by the editor without benefit of a review. Why? We never found out. We made an appeal to the journal for a review which was finally made, leading to the eventual and belated publication in 1961.

"I like to think of the work as the first significant example of an engineering application of modern thermodynamics of fluid phase equilibrium which in this instance made possible the replacement of voluminous charts with a few equations which did more and better. Many more fine applications followed rapidly.

"I think the reason that this paper is widely cited is that it offers a neat computer solution to a problem of long standing and enduring interest. Subsequent progress can be found in a recent monograph, *Equations of State in Engineering and Research.*"[1]

1. Chao K C & Robinson R L, Jr., eds. *Equations of state in engineering and research.*
Washington, DC: American Chemical Society, 1979. 466 p.

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